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HEAT-SHIELDING MATERIAL BASED ON CERAMIC REINFORCING FILLERS

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A technology for manufacturing intermediate fiber products based on aluminosilicate fibers, making it possible to obtain uniform-density mats from 20 to 40 vol.% and obtaining heat-shielding material with adjustable volume fraction of reinforcing filler, is described. The thermal conductivity and phase stability of samples of Gelarm heat-shielding material based on oxide fibers and an aluminosilicate matrix modified by components that retard crystallization and sintering of the reinforcing fibers are presented.

Key words: heat-shielding material, glass ceramic composite material (GCCM), fibers, thermal conductivity, phase stability.

The use of heat shielding in modern fourth – fifth generation aerospace technology toughens the requirements on the materials being developed for working temperatures to 1650°C and structural strength to 100 MPa. Heat-shielding glass ceramic composite materials (GCCM) are widely used to obtain the functional characteristics of modern aircraft.

Fibrous composite materials based on ceramic and glass ceramic matrices attract attention because they are extremely stable against thermal and chemical actions. They have demonstrated a number of advantages over metallic materials, specifically, a unique combination of low density with high structural strength, stability, and a number of other properties [1].

The requirements for withstanding oxidation at high temperatures limit considerably the choice of reinforcing ceramics and ceramic fibers. Oxide ceramic is most promising for synthesis of high-temperature heat shielding; in addition, the reinforcing components of oxide ceramic are not in short supply or expensive. Fibers based on aluminum oxide, mullite and zirconium dioxide as well as silicon nitride and carbide are considered to be promising. As a rule, the same compounds are used to synthesize the matrix; this has a favorable effect on their compatibility with the reinforcing filler. The performance of composite oxide materials can be enhanced by improving the quality of the initial raw material and optimizing the compositions and technological regimes [2].

The properties of such materials can be adjusted by finding suitable components and their quantitative ratios, distribution and orientation in the interior of the material as well as their technological production parameters. This makes it possible to obtain multifunctional composite materials.

In the present work, the system Al_2O_3–SiO_2 was studied for the matrix. Aluminum oxide was introduced into the matrix in the form of water-soluble salts or fine powder. A distinguishing feature of glassy and glass-ceramic matrices is that they possess low reactivity and high resistance to deformation in the solid-phase state. However, the problems of chemical and mechanical compatibility for composites are very serious and can only be solved by careful scientific and practical development work on the synthesis and technological processes.

One of the most important stages in the production of GCCM and securing high-performance properties is obtaining a high-quality intermediate product — a mat comprised of volume-structured reinforcing fillers. A mat must have uniform density at the macro and micro levels and maximum isotropy, and it must have the required technological strength and prescribed geometric dimensions. A scheme for the next process in the production of the GCCM must already be taken into consideration at the mat production stage.

The technology for fabricating mats from reinforcing fibers based on mullite and kaolin was developed. It includes the following production stages:

– mechanical cleaning;
– preparation of a water suspension;
– pouring the water suspension into a mold;
– removing liquid from the mat;

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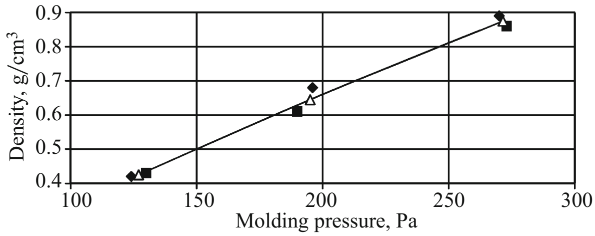

Fig. 1. Effect of molding pressure on the density of fibrous intermediate products.

TABLE 1. Shrinkage of GCCM panels

GCCM fibers	Al_2O_3–SiO_2 matrix modifiers	Panel linear shrinkage, %
Mullite	No modifiers	10 – 11
	B_2O_3 + MgO	3 – 5
SiC FC	No modifiers	2 – 5
	B_2O_3 + MgO	0 – 2

– drying the intermediate product.

The mechanical cleaning of the initial reinforcing fibers consisted of removing large non-fibrous inclusions. When fibers based on SiC filamentary crystals (SiC FC) are used iron impurities must be removed from them by treatment with hydrochloric acid.

The water suspension was prepared in a tank with milling bodies in a ball mill. In the process of preparing the water suspension it was found that during mixing a fiber undergoes chaotic collisions with the milling balls, as a result of which up to 50% of the initial mechanical characteristics are lost. For this reason, a variant of the preparation of water suspensions from fiber processed in cutting mill was tested. The mats obtained from fiber processed in a cutting mill were more workable and mechanically stronger.

Water can be removed spontaneously and under pressure. Pressure regulation made it possible to obtain mats from 20 to 40 vol.% as well as cermic material with volume fraction of the reinforcing filler adjustable from 20 to 40%. The mats have a uniform density with no lamination. Data on the density change of the fibrous blanks obtained as a function of pressure are presented in Fig. 1.

The drying process completely removed all moisture from the mat by allowing the moisture to evaporate. The temperature–time regime for mat drying is the determining factor in obtaining defect-free intermediate products; there must be no warping, separation or cracks.

The principal method of obtaining GCCM based on fibrous intermediate products from oxide and silicon carbide fibers and a glass ceramic matrix is the sol-gel method. Advantages of this method are its low energy-intensiveness and the high quality of the material. There are various possible technological techniques for obtaining GCCM, ranging from simple permeation of a fibrous blank by a matrix composition to hot molding the intermediate GCCM product under pressure.

At the transition stage from fabricating samples to fabricating articles from GCCM the dependence of the quality and property stability of the articles on many factors was taken into account: the properties and quality of the initial components, process parameters and dimensions and configuration of the manufactured article. Often, different kinds of surface and internal defects in the ready article at the transition stage, which were not observed during the fabrication process, were taken into account. As a rule, the number of defects increased with increasing size of the article and with the type of heat treatment used on the article.

To eliminate the defects associated with the disruption of phase stability the GCCM, agents — crystallization inhibitors (boron-containing components) — were introduced into the gel matrix, and magnesium oxide, which slows down the sintering of glass-ceramic fibers, was introduced to reduce shrinkage during high-temperature heating [3].

Experimental studies confirmed the correctness of the directions chosen. Six batches of 400 × 400 × 150 mm panels were made from Gelarm heat-shielding materials based on fibers of the systems SiC, $3Al_2O_32SiO_2$ and matrix in the system Al_2O_3–SiO_2 with B_2O_3 and MgO additions. The experimental panels underwent preliminary heat treatment to temperature 1000°C for 1 h, after which they were tested for temperature stability at the 1650°C for 20 min and 1 h. The temperature stability of the panels was evaluated according to the change of their dimensions and surface quality.

The data on the shrinkage of the GCCM panels are presented in Table 1.

The introduction of modifiers into the matrix increased the temperature stability of the GCCM 2 – 2.5-fold.

XPA confirmed the temperature stability of the experimental GCCM panels based on oxide reinforcing fibers. The phase composition of the GCCM samples was studied in the initial state and after heat-treatment using the following regimes: at 1000°C for 10 min, 1 h and 1650°C for 10 min, 1 h. The samples were studied in a D/Max-2500 diffractometer (Rigaku Company) with copper monochromatic radiation (Fig. 2).

The studies established that the principal phases of the initial GCCM are corundum Al_2O_3, amorphous quartz SiO_2 and the oxide Al_2O_3. An additional phase — mullite — and a very small amount of sillimanite (< 0.55%) appear on heating to 1000°C for 1 h. When the material is heated to 1650°C and soaked for 1 h the main composition of the GCCM remains unchanged, the mullite content does not change, the content of amorphous quartz (< 0.1%) decreases only very little and crystalline quartz appears.

The thermophysical properties of the GCCM based on oxide fibers and made from filamentary silicon carbide crystals (SiC FC) were studied. The experimental samples were 0.015 m in diameter and 0.003 m thick. Their density was γ = 0.6 – 0.7 g/cm^3.

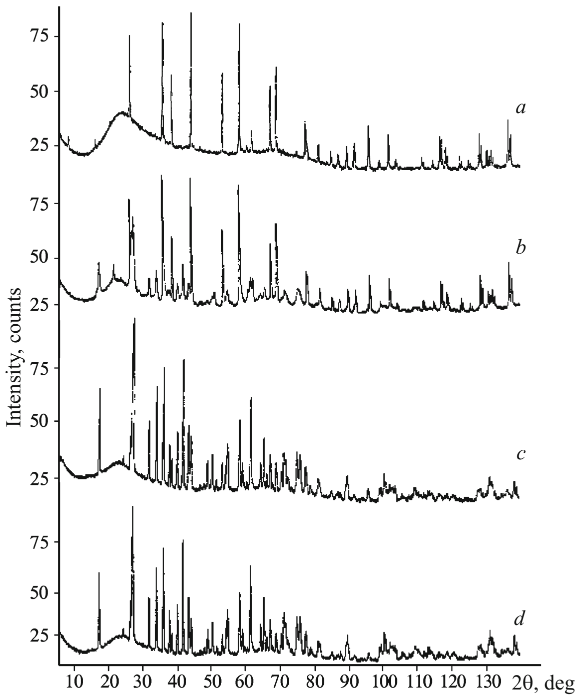

Fig. 2. Diffraction patterns of Gelarm GCCM samples based on oxide fibers: *a*) initial sample; *b*) after heat-treatment at $t = 1000°C$ for 1 h; *c*, *d*) after heat-treatment at $t = 1650°C$ for 10 min and 1 h, respectively.

The following data were obtained: the thermal conductivity λ of the samples based on Al_2O_3 –SiO_2 system was $0.13 - 0.14$ W/(m · K) while that of the samples based on SiC FC was $0.24 - 0.25$ W/(m · K). The results of the studies show that the GCCM developed on the basis of thermal conductivity surpasses GCCM based on SiC reinforcing fiber, which is in short supply.

The GCCM samples based on mullite and silicon carbide fibers were tested in the plasmatron at the M. M. Gromov Flight Test Institute in the temperature interval 1000 – 1400°C; the results were positive.

The main structural and performance indicators for the GCCM developed on the basis of oxide reinforcing fillers and a glass ceramic matrix are: high temperature stability and mechanical strength, low thermal conductivity and density and ecological safety.

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